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(54) Composite Material and a
Process for Manufacturing the
Same

(57) Composite materials consisting of
reinforcing fibres and a temperature-

resistant flameproof binder,
characterised in that the binder used
is a hybrid matrix consisting of a
soluble thermoplastic high polymer
and thermosetting resin.

Certain of the chemical formulae
appearing in the printed
specification were submitted in
formal form after the date of
filing.

GB 2 060 490 A

SPECIFICATION

Composite Materials and a Process for Manufacturing the Same

The invention relates to composite materials which consist of fibres, e.g. glass fibres, carbon fibres or aromatic polyamide fibres (referred to as aramide fibres) in the form of fleeces, woven fabrics or knitted fabrics and a temperature-resistant matrix, i.e. a matrix which is non-combustible; the invention furthermore relates to a process of producing such composite materials.

The main field of application of the composite materials according to the invention resides in their use as structural components, as thermal and electrical insulators and as fireproofing materials.

It is known that high-strength and thermally stressable composite materials employing temperature-resistant resins or polymers can be produced in that the impregnating resin is dissolved in a solvent to produce an impregnating lacquer whereupon fibrous materials such as carbon fibres, glass fibres, boron fibres or organic high-module fibres consisting of aromatic polyamides (referred to as aramides) in the form of fleeces, woven fabrics or knitted fabrics, after which the solvent is evaporated off to leave a pre-impregnated fibre material (referred to as a prepreg) which can be worked under pressure and at high temperatures to produce temperature-resistant fibre laminates.

U.S. Patent No. 3,179,614 describes linear fully aromatic polyimides which, via soluble pre-products, polyamido carbonic acids, can be processed into laminates in that imidisation is carried out under high temperatures and under pressure. When the polyamido carbonic acid is transformed into the fully aromatic polyimide, this reaction takes place in the temperature range between 220 and 300°C, water is released which leads to pores forming in the laminate. Pores in the matrix do however impair the mechanical properties of the composite fibre materials and do not permit of full utilisation of the mechanical properties inherent in the fibres. This complex of problems led to the development of thermosetting polyimide resins which are known for instance from French Patent Specifications Nos. 1,455,514 and 1,555,564 and German Offenlegungsschriften Nos. 2,530,571, 2,754,632, 2,754,631 and U.S. Patent Specifications Nos. 3,839,287, 3,689,464 and 3,562,223.

The resins of the cited patents and Offenlegungsschriften have in common that during hardening, i.e. during the transition from the monomeric to the polymeric condition, no products of condensation are released which might lead to pore formation when the resins are used for the production of fibre laminates. Disadvantageous when the resins of the above-mentioned patents and Offenlegungsschriften are used however is the fact that high boiling, high-polar solvents are required in order to produce the impregnating solution, due to the solubility properties of the resins. On account of their ready affinity for the resins, these solvents can only with great difficulty be completely removed from the laminates. The residual solvent remaining in the laminates after hardening disadvantageously and particularly at high temperatures has a softening effect and in the end results in a considerable deterioration of the mechanical properties at high temperatures.

According to the state of the art, it is furthermore known that thermoplastic polymers, for example polysulphones, can be used as a matrix for fibre laminates. These fibre laminates are manufactured in that pre-impregnated fibre materials (referred to as prepreps) having a very low content of thermoplastic polymer of about 10 to 15% and films of thermoplastic polymers are alternately layered in a heated panel press and are moulded under pressure and at temperatures above the melting point of the thermoplastic prepreg to produce an homogeneous pore-free laminate. Essential to the application of this technology however is the solubility of the thermoplastic resin in suitable solvents for the casting of films and the genuine fusibility of the linear polymer. Naturally, by reason of the soluble binder, such laminates are susceptible to solvents; for application at high temperatures, for example 250°C, melting points of around or above 350°C are required (literature: Phillips & Murphy, RAE Technical Report No. 76140, October 1976). However, it has been surprisingly found that mixtures of morphological thermoplastic soluble polymers and thermo-setting resins can be substantially processed to produce solvent-free films or that these films can be used for manufacturing fibre laminates in that the cited technology of the moulding of polymer films and low-resin prepreps is carried out in the press at high temperatures.

The advantage of this procedure lies in the fact that on the one hand completely solvent-free and pore-free laminates are provided and in that the laminates obtained are after hardening resistant to solvents by reason of the proportion of thermosetting highly cross-linked imide.

A further progressive feature lies in the fact that it is possible via the content of thermosetting resin fusible at low temperatures to regulate the flow properties during moulding; i.e., the films fuse according to the melting point and content of thermosetting resin.

At the moulding stage, therefore, relatively low processing pressures are required.

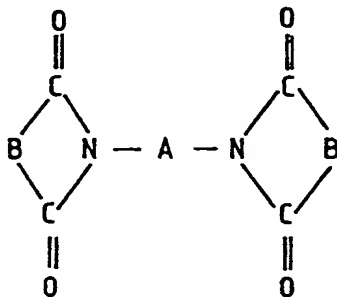
The object of the present invention is to provide composite materials consisting of fibres such as for example glass fibres, carbon fibres, boron fibres or aromatic polyamide fibres in the form of fleeces, woven fabrics or knitted fabrics and a temperature flame-resistant binder, characterised in that the binder used is a hybrid matrix consisting of a soluble thermoplastic high polymer and a thermo-setting resin.

A preferred embodiment is characterised in that the ratio of thermoplastic polymer to thermosetting resin in the hybrid matrix is between 95:5 and 5:95.

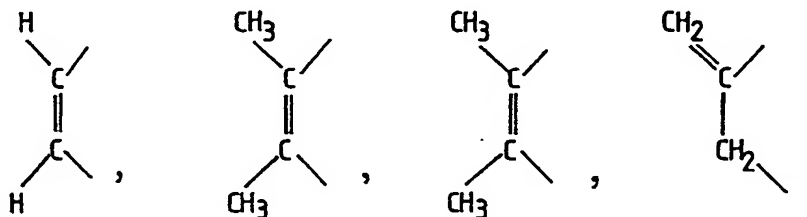
The thermoplastic component of the hybrid matrix is preferably a soluble temperature-resistant high polymer chosen from polysulphone, polyhydantoin, polycarbonate, polyamide, polyimide, polyamide imide, polyphenyl quinoxalin, polybenzimidazol, polyoxadiazol or polybenzoxazol.

- 5 A further preferred embodiment is characterised in that the thermosetting component used in the hybrid matrix is a soluble temperature-resistant resin selected from polyester, epoxy resin, bismaleic imide or a prepolymer comprising terminal acetylene groups.

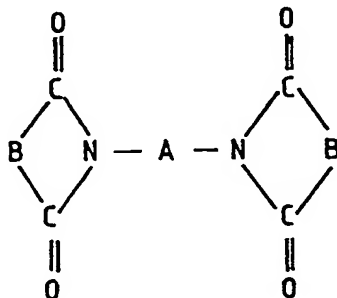
- 10 A further preferred embodiment is characterised in that the thermoplastic component used in the hybrid matrix is a polyamide imide obtainable from benzophenone-tetracarboxylic dianhydride, m-amino benzoic acid and diamino diphenyl methane and in that the thermosetting component employed is a bismaleicimide to the general formula



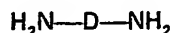
in which the radical A denotes a bivalent organic radical having at least two carbon atoms while B is a bivalent organic radical according to the following formulae



- 15 A further preferred embodiment of the composite materials according to the invention is characterised in that the thermoplastic component used is a polyether sulphone and in that the component used as a thermosetting component is a polyimide prepolymer which is obtainable by reaction of a bismaleic imide to the general formula



- 20 with a diamine to the general formula



in which D is a bivalent organic radical with at least two carbon atoms, the molar ratio between bisimide and diamine being preferably between 1.2 and 5.

- 25 Furthermore, the present invention relates to a process for producing composite materials consisting of fibres such as for example glass fibres, carbon fibres, boron fibres, aromatic polyamide fibres, in the form of fleeces, woven fabrics or knitted fabrics and a temperature-resistant flameproof hybrid matrix consisting of a thermoplastic high polymer and a thermosetting resin which is characterised in that films of the hybrid matrix and low resin prepreg of the hybrid matrix are alternately layered and are moulded under pressure and at high temperatures.

- 30 The composite materials are preferably manufactured in that solvent-free films of the hybrid matrix system in which the thermosetting resin is contained in unhardened largely monomeric

condition are alternately layered in a press with prepregs containing substantially 5 to 20% of the hybrid matrix system followed by moulding under pressure at temperatures at which the thermosetting resin is transformed into the liquid state after which cross-linking is carried out under pressure and at high temperature.

5 The individual steps in the process of producing composite materials from a hybrid thermoplastic- thermosetting matrix are preferably as follows: 5

a) production of hybrid films consisting of a thermoplastic high temperature polymer and a thermosetting polyimide resin in the non-hardened condition;

b) production of a prepreg consisting of the pre-orientated fibres in the form of rovings, woven 10 fabrics, knitted fabrics or fleeces and the hybrid matrix, the resin content amounting to substantially 15%, 10

c) moulding of the films and prepregs under pressure to produce a laminate having high mechanical properties and high thermal stability.

The individual procedural steps and products which are preferably used for the new technology 15 are described in detail hereinafter. 15

A condition essential to application of the new method to the production of improved high temperature laminates is the facility to produce hybrid films consisting of the thermoplastic high temperature polymer and the thermosetting high temperature resin.

It is the function of the thermoplastic polymer to impart the necessary mechanical stability to the 20 film. 20

In principle, any thermoplastic film-forming polymers may be used if it is possible also to produce from them low resin prepregs, via the use of solvents.

For high temperature-resistant laminates, high temperature-resistant thermoplastic polymers are used, for example polysulphones, aromatic polyamides, polysulphones, aromatic polyamides (sic!), 25 polyamidimides, polyimides, polyphenol quinoxalines, polyquinoxalines, polyaxadiazoles, 25 polythiadiazoles.

Already known from U.S. Patent No. 3,708,458 are copolyimides which are readily soluble in organic solvents such as dimethyl formamide, dimethyl acetamide and N-methyl pyrrolidone and which can, out of these solvents, be poured to produce films.

30 Hybrid films are produced in that both the thermosetting and also the thermoplastic resin are dissolved in a solvent suitable for both resins and in that a film is produced on a carrier by pouring and drying. 30

It is a further aspect of the feasibility of the new process that prepregs having a resin content of between 5% and 20% can be produced via a solution of the hybrid matrix which in the case of soluble 35 polymers is brought about in that fibres in the form of woven fabrics, knitted fabrics, rovings or fleeces are pulled through the solution so that the fibres are impregnated, excess resin is allowed to run off and 35 in that the impregnated fibre material is liberated from solvents by drying, for example in a circulating air cabinet.

The new composite materials are then easily produced in that alternate layers of prepregs and 40 hybrid films are prepared and in that the stack of alternate layers is hardened in a heated panel press under pressure and at a temperature of for example between 170 and 280°C. 40

A laminate is thereby obtained, the hybrid matrix functioning as a binder. The laminates are pore-free and exhibit good mechanical properties even at temperatures of around 250°C.

The following examples will serve as a further explanation of the substance of the present 45 invention. 45

Example 1

The following are used as raw materials for the production of a glass fabric laminate:

a) a linear morphologically thermoplastic polyamide imide (PAPI) produced from benzophenon tetracarboxylic dianhydride, m-amino benzoic acid and 4,4'-diamino diphenyl methane. The 50 polyamide imide is soluble in dimethyl formamide, dimethyl acetamide and N-methyl pyrrolidone and has an inherent viscosity of 0.5 dl/g. 50

b) 4,4'-bismaleic imido diphenyl methane as a thermosetting imide resin.

c) glass fabric of the Atlas type with a weight per unit of area of 290 to 310 g/sq.m, furnished with a commercially available amino silane adhesion promoter.

55 6.15 g of the thermoplastic polyamide imide are dissolved in 55.35 g dimethyl formamide; furthermore, a solution of 6.15 g 4,4'-diamino diphenyl methane in 55.35 g dimethyl formamide is produced. 55

Both solutions are combined; the result is a 10% solution of the hybrid matrix in dimethyl formamide. This solution is used to produce a poured film by pouring the solution onto a crystal glass 60 plate measuring 400x400 mm. The solvent is eliminated by drying for 3 hours at 60°C and for 18 hours at 75°C to the extent that the film can be pulled off the glass sheet. After drying in a circulating air drying cabinet for 19 hours at 70°C, the film has a residual solvent content of 8.5%. 60

Furthermore, a 15% solution of the hybrid matrix in dimethyl formamide is produced, the ratio of thermoplast to duroplast being 1:1.

Prepared glass fabric blanks measuring 150x150 mm are impregnated by being dipped in the solution of hybrid matrix, excess solution being allowed to run off and the prepregs being dried for 18 hours at 70°C in a circulating air drying cabinet. After one dip, prepregs are obtained which have a resin content of hybrid matrix of 9 to 10%, while two dips result in a resin content of 16 to 17%. The residual solvent content of the prepregs is 0.75%.

In order to produce a glass fabric laminate, 8 glass fabric prepregs and 9 hybrid films are placed in alternate layers between two aluminium films and are hardened in a heated panel press at 220°C and under a pressure of 40 Kp/sq.cm for three hours, after which the result is cooled, removed from the mould and heat treated for 15 hours at 250°C.

The resultant laminate has the following properties at room temperature:

Fibre content	45 per cent by volume
Resin content	55 per cent by volume
Density	1.82 g/cu.cm
Bending strength	48 Kp/sq.cm (DIN53452)
Bending modulus	1930 Kp/sq.cm (DIN53452)
Interlaminar shearing resistance	4.5 Kp/sq.cm

At 250°C, the residual strength is still 70% of the starting value.

Example 2

The procedure described in Example 1 is used in order to produce a pore-free dense temperature-resistant glass fabric laminate. Instead of the polyamidimide, a copolyether sulphone is used as the thermoplastic constituent of the hybrid matrix. By virtue of the good film forming properties of the polysulphone due to the high molecular weight, the thermoplast/duromer ratio as 1:2.

As in Example 1, 4,4'-bismaleic imido diphenyl methane is used as the thermosetting resin. Hardened at 210°C and 40 Kp/sq.cm, the laminate exhibits the following properties:

Fibre content	50 per cent by volume
Density	1.0 g/cu.cm
Bending strength	52 Kp/sq.cm
Bending modulus	2150 Kp/sq.cm
Interlaminar shearing resistance	5.8 Kp/sq.cm

At 200°C, the mechanical strength properties are still 50% of the values at room temperature.

Example 3

A thermoplastic polyimide produced according to U.S. Patent No. 3,708,458, Example 1, and a thermosetting polyimide resin according to German Offenlegungsschrift No. 2,530,571, Example 1, are used in order to produce a carbon fibre fabric laminate, the said imide resins forming the hybrid matrix.

A poured film is produced via a N-methyl pyrrolidone solution of the hybrid matrix. The weight ratio of thermoplastic polyimide to duro-plastic polyimide is 2:1. Prepregs with a resin content of 10% are produced via a 15% solution of the hybrid matrix in N-methyl pyrrolidone by dipping. Excess resin is allowed to run off and the prepregs are dried for 15 minutes at 140°C in a circulating air drying cabinet. The residual solvent content is 2.1%.

Films of the hybrid matrix and prepregs, produced as described, are layered alternately and hardened in a panel press at 50 Kp/sq.cm pressure and at a temperature of initially 190°C rising to 240°C, for a period of 4 hours.

The laminate exhibits the following properties:

Density	1.50 g/cu.cm
Bending strength	62 Kp/sq.cm
Bending modulus	6800 Kp/sq.cm.

68% of the starting strength is still measured at 250°C.

Within the framework of this disclosure, the expression "prepregs" stands for "pre-impregnated fibre materials".

Claims

1. Composite materials consisting of reinforcing fibres and a temperature-resistant flameproof binder, characterised in that the binder used is a hybrid matrix consisting of a soluble thermoplastic high polymer and a thermosetting resin.

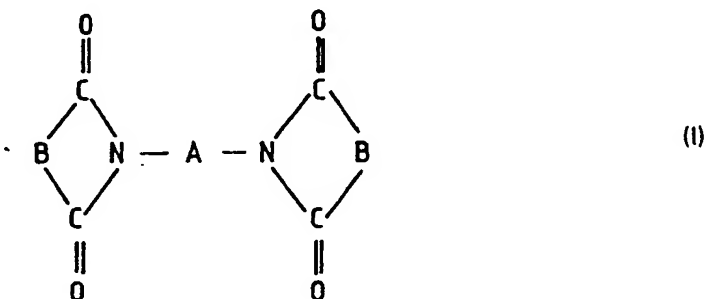
2. Composite materials according to Claim 1, characterised in that the ratio of thermoplastic polymer to thermosetting resin in the hybrid matrix is between 95:5 and 5:95.

3. Composite materials according to Claim 1, characterised in that the thermoplastic component

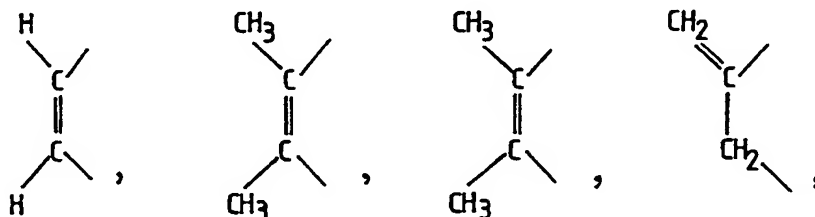
used in the hybrid matrix is a soluble temperature resistant high polymer chosen from polysulphone, polyhydantoin, polycarbonate, polyamide, polyimide, polyamide imide, polyphenyl quinoxalin, polybenzimidazol, polyoxadiazol or polybenzoxazol.

4. Composite materials according to claim 1, characterised in that the thermosetting component
5 used in the hybrid matrix is a soluble temperature-resistant resin chosen from polyester, epoxy resin, bismaleic imide or a prepolymer comprising terminal acetylene groups.

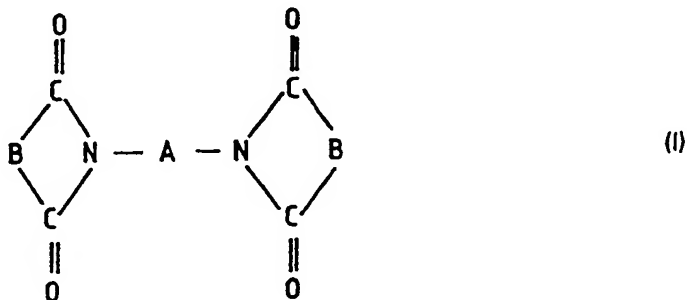
5. Composite materials according to Claim 1, characterised in that the thermoplastic component
10 used in the hybrid matrix is a polyamide imide obtainable from benzophenone-tetracarboxylic acid dianhydride, m-amino benzoic acid and diamino diphenyl methane and in that the thermosetting component employed in a bismaleic imide to the general formula



in which the radical A denotes a bivalent organic radical having at least two carbon atoms while B is a bivalent organic radical according to the following formulae



6. Composite materials according to Claim 1, characterised in that the thermoplastic component
15 used is a polyether sulphone and in that the component used as a thermosetting component is a polyimide prepolymer which is obtainable by reaction of a bismaleic imide to the general formula



with a diamine to the general formula

- 20
$$\text{H}_2\text{N}-\text{D}-\text{NH}_2$$
 (II) 20

in which D is a bivalent organic radical with at least two carbon atoms, the molar ratio between bisimide (I) and diamine (II) being preferably between 1.2 and 5.

7. Composite materials according to Claim 1, wherein the fibres are glass fibres, carbon fibres, boron fibres or aromatic polyamide fibres in the form of fleeces, woven fabrics or knitted fabrics
25 characterised in that films of the hybrid matrix and low resin prepregs of the hybrid matrix are alternately layered and are moulded under pressure and at elevated temperatures.